

NEW STARCH-BASED POLYMER TECHNOLOGIES

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INTRODUCTION

For several years our Center has conducted both fundamental and applied research to develop new products from starch. These research efforts have resulted in several new technologies and new markets for starch and have led to additional applied research by the private sector in many countries. Some of the earlier efforts involved depolymerization of starch into heat- and alkali-stable polyols, and subsequent studies involved how to use these as polyol initiators to make new polymers for polyurethane (ref.1), alkyd resin (ref.2), surfactant (ref.3), adhesive, and food emulsifier applications. With the advent of the petroleum crisis, these studies and those of other research laboratories have become of special interest to the private sector seeking to find less expensive renewable substitutes for petroleum. The 0.5-billion-lb/yr U.S. rigid polyurethane foam industry has converted to carbohydrate-based polyol initiators, and the surfactant and alkyd industries are looking more toward natural polyols and away from petroleum. One U.S. starch company recently constructed a 30-million-lb/yr facility for making starch-derived polyols; a company executive said that such starch-derived chemicals could prove to be a 5-billion-lb/yr market, primarily for foams, films, adhesives, and paints (ref.4).

This paper describes concepts, approaches, and some results of current programs at our Center on new starch polymer technologies to provide biodegradable plastics, membranes, and controlled release systems. The research is intended to help reduce pollution associated with the disposal of nondegradable plastics, to lower the level and frequency of application and improve safety in handling of agricultural chemicals, and to reduce U.S. dependence on imported petroleum. Approaches are toward polymer blending, grafting, and crosslinking of starch in aqueous systems and away from major modifications with toxic and flammable chemicals that might discourage the private sector from making the technology available to consumers. The studies

take advantage of the natural polymeric structure and the superior biodegradability of starch over most petroleum-derived polymers. The water sensitivity of starch offers advantages for some applications, whereas for some others this water sensitivity must be reduced. Although the amylose fraction of starch would offer certain property advantages, we have restricted our current programs to whole starch because of the cost and the restricted availability of amylose.

STARCH IN PLASTICS

Different approaches have been investigated for using starch in plastics. One approach, using starch as a dry particulate filler, has been investigated extensively both in plastics and in rubber. A second approach, the one we are now investigating, involves using gelatinized starch molecules as an integral part of the polymeric structure. Starch is inherently water sensitive; upon drying it becomes rigid and brittle from the high densities of molecular branching and hydrogen bonding. The embrittlement imparted to plastics by starch is overcome to various degrees by adding plasticizers and other materials that retard association of starch molecules.

Plasticized starch films

The only successful plasticizers for starch films are water-soluble materials that help retain moisture in the film. Water dispersions of starch and plasticizers, such as glycerol, can be cast into flexible films. However, they have no industrial potential as nonsupported films because they deteriorate in water and become very brittle at ambient conditions. Film flexibility and water resistance were greatly improved by adding polyvinyl alcohol (PVA) to the starch-glycerol formulation and by coating the films with a thin layer of either poly(vinyl chloride) or a vinylidene chloride-acrylonitrile copolymer (ref.5).

Noncoated films made with PVA, glycerol plasticizer, and high levels of starch rapidly lose flexibility. For example, films made with 22.4% glycerol, 15% PVA, and 60% starch could be stretched or elongated 146% after aging 1 day, but they elongated only 9% after 10 days aging. Increasing the glycerol level to 30% and decreasing the starch level to 51% increased elongation to 300%, but effects of the plasticizer decreased rapidly with aging. In contrast, mixed polyol plasticizers composed of either 3 parts glycol glucoside or sorbitol to 1 part glycerol yielded films with % elongation stabilized for more than a year. Similar results were observed when CaCl_2 was added to a glycerol plasticized film.

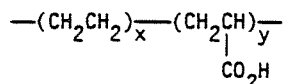
The reason polyols plasticize starch films is not fully known but may relate to their moisture-holding power or humectancy. At high moisture content,

sufficient water is present to satisfy the hydrogen-bonding sites of starch. As films age and lose moisture, added polyols may satisfy some of the bonding capacity but in so doing they lose some of their humectancy.

These studies on plasticized starch-PVA films led to the commercialization of water-soluble films made by band-casting aqueous solutions of water-soluble starch, PVA, and plasticizers. These films are now used to produce laundry bags for use by hospitals to protect patients and hospital personnel against the danger of cross contamination from soiled linens. Laundry sealed in the bags is placed directly into washing machines, where the bag dissolves.

Nonplasticized starch films

The blending of starch with synthetic polymers and water-soluble plasticizers is proving very successful for specific applications of starch-based film because the benefits of water solubility exceed the high cost of film casting, where production rate is slow and large amounts of processing water must be evaporated. For larger scale applications, water-extractable plasticizers must be avoided, and the formulation must be adaptable to the more economically feasible extrusion blowing technique now used for most synthetic film production. Also, at least 40% starch must be present to achieve a desirable rate of biodegradation. We are having considerable success in achieving these objectives by blending gelatinized starch with poly(ethylene-co-acrylic acid) (EAA).



Films made from this system require no plasticizer, yet they remain flexible even after exposure to water and drying. Fig. 1a is a photomicrograph of a dry, flexible film that contained 50% partially gelatinized starch and 50% EAA. The starch appears reasonably well dispersed into the film. Although the mechanism is not known, we envision that as internal bonding within starch molecules is reduced during gelatinization and extrusion, new bonds are formed with the EAA carboxyl group that retard retrogradation of the starch. The dried film may correlate with the theory of "molecular slippage" relief of locally high stresses associated with elastomer reinforcement. In essence, that theory asserts that physically adsorbed chains on filler particles slip or break the physical bond in areas of high stress to more uniformly distribute stress throughout the sample (ref.6). Under stress, the starch chains may not be broken or totally disbonded from the EAA since other portions of a "slipped" chain can remain hydrogen bonded to the EAA.

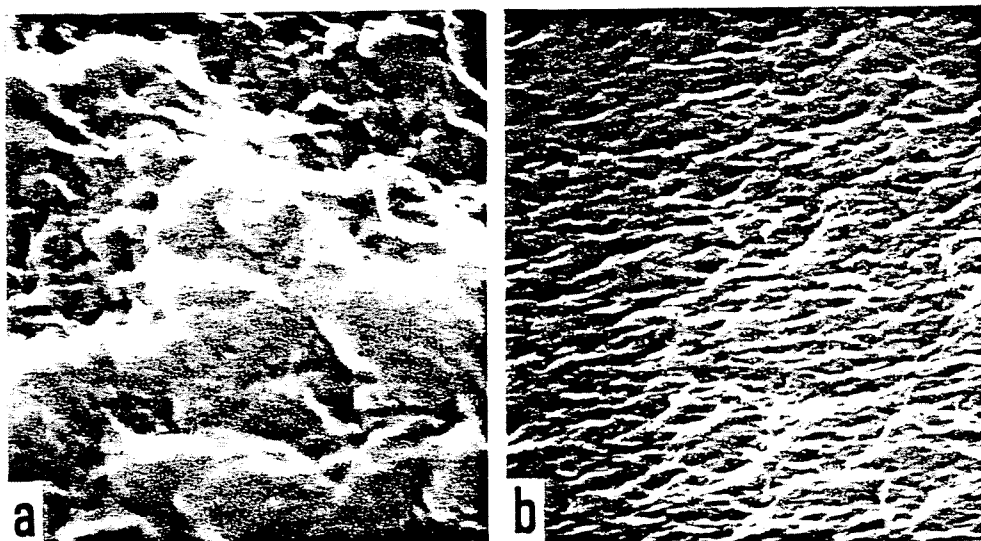


Fig. 1. Scanning electron photomicrographs of film specimens containing 50% starch and 50% EAA. Samples photographed at 10,000 times. (a) No NaOH added (b) 5 pph NaOH added.

In addition to eliminating the requirement for water-soluble plasticizers, the starch-EAA system is the first reported blend with up to 50-60% starch that can be extrusion-blown into films. These films have several potential applications where biodegradability is important, such as in agricultural mulch. Carnell (ref.7) reports the following consumption of plastic mulch, million lb/yr: Japan, 250; U.S., 100; France, 84; and Israel, 16. Plastic mulch is used on such crops as tomatoes, peppers, melons, and sweet corn to help control soil moisture and temperature, reduce nutrient leaching, prevent weed growth, and increase crop yields by 50 to 350%. Polyethylene film does not degrade between growing seasons, so it must be removed from the field and buried or burned at an estimated cost of \$100 per acre.

Semipermeable membranes

Adding a strong alkali, such as sodium hydroxide, to the starch-EAA blend will cause extrusion-blown films from the blend to have semipermeable characteristics. The photomicrograph (Fig. 1b) of a dry film specimen, made from a blend that contained on a dry basis 50% starch, 50% EAA, and 5 parts per hundred (pph) NaOH, illustrates a much better dispersion of the starch than was achieved without alkali (Fig. 1a). Preliminary evaluation of the films is being made with a rotating dialysis cell. This cell consists of two hollowed-out discs that are clamped together, with the membrane to be tested

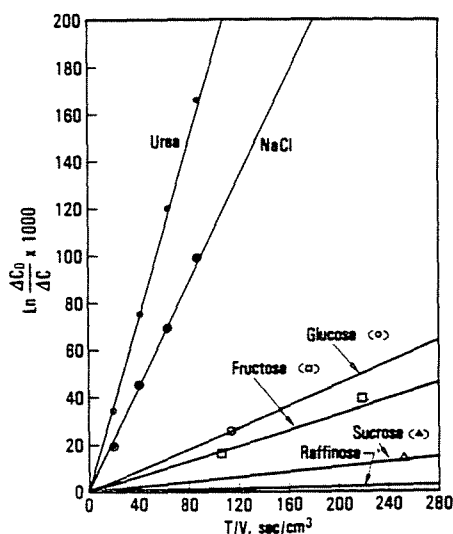


Fig. 2. Relation of $\ln \Delta C_0 / \Delta C$ vs. t/v for six solutes diffusing through a film containing 40% starch (fitted by equation 2).

separating the two discs. One of the resulting cylindrical compartments is partially filled with water and the other with solution, and while diffusion proceeds the cell is rotated about its horizontal shaft at a constant speed of 73.5 rpm. Observed membrane permeabilities (P_0) are calculated from the rate of change of the solute concentrations in both compartments, using the following equation:

$$P_0 = \frac{\ln(\Delta C_1 / \Delta C_2)}{A(1/V_a + 1/V_b)(t_2 - t_1)} \quad (1)$$

where ΔC is the measured difference in concentration between the two chambers at conveniently separated times of measurement t_1 and t_2 , A is the membrane area through which transport takes place, and V_a and V_b are the total volumes of each of the two chambers. The equation predicts a straight line passing through the origin where $\ln(\Delta C_0 / \Delta C)$ is plotted against t/v , when the volumes

$$\ln(\Delta C_0 / \Delta C) = b(t/v) \quad (2)$$

on each side of the film are kept equal but are decreased during time studies due to sampling for analyses. Experimental data from a film containing 40% starch, 60% EAA, and 5 pph NaOH are plotted in Fig. 2 where three or four samples of the solutions on each side of the film were analyzed after various times of dialyses. Area of the exposed film was 78.5 cm², and 1.5% solute concentrations were used for each run. The data are consistent with a zero theoretical intercept.

Figure 2 clearly demonstrates that the films allow small molecules of urea and NaCl ions to diffuse many times faster than larger sugar molecules.

The slower permeability rate for NaCl relative to urea may be attributable to charges on the film.

Table 1 lists additional permeability data, where the NaCl and urea rates were determined on individual runs and the sugars and alanine were run as mixtures and analyzed by HPLC. Increasing the starch level or adding water-soluble materials such as ethylene glycol or sucrose increased diffusion rate. The water-soluble additives are readily leached during film soaking, so their primary functions may be to increase the starch to EAA ratio in the soaked film; they also improve ease of film preparation. Most of the data reported in Table 1 were collected on film samples that had soaked in water for several days. We have since learned that transport rates decrease during water soaking for up to 30 days. However, studies underway reveal that the films can be treated with alkaline solutions to restore the transport rate and in some instances increase the rate by severalfold.

TABLE 1
Permeability data for several solutes^a

Starch/ EAA, % ^b	$P_o \times 10^6$ (cm/sec)						
	NaCl	Urea	Glucose	Fructose	Sucrose	Raffinose	Alanine
60/40	31.6	53	6.3	--	2.9	2.5	--
40/60	5.1	17.5	0.9	1.2	0.6	0.1	2.4
20/80	--	0.01	--	--	--	--	--
40/60 ^c	4.6	--	1.0	1.1	0.4	0.1	2.2
40/40 ^{c,d}	11.8	33.6	2.0	2.3	0.9	0.2	4.0
40/30 ^e	34.7	112	5.1	5.7	2.6	1.3	6.5

^aSolute concentrations were 1.5%; ran at atm pressure and room temperature.

^b5 parts NaOH per 100 parts of starch-EAA were added to formulation.

^cHydroxyethylated starch.

^dFormulation contained 20% ethylene glycol.

^eContained 30% sucrose.

It is too early to predict how starch-based films may fit into the projected \$1.7 billion per yr semipermeable membrane field (ref.8). Economically, they have a good chance of commercial acceptance because they can be produced by the low-cost extrusion blowing technique, and formulation variables allow a wide range of transport rates and pore size. Current

application of membranes include: gas separation, such as separating hydrogen from ammonia; wastewater treatment; controlled release of materials, such as drugs; and various dialysis applications for the kidney machine or, industrially, for separating large molecules from smaller ones.

Starch graft copolymers

Fanta and Doane (ref.9) have reviewed starch grafts for several applications. The grafting of synthetic polymers onto starch provides another approach for making starch-based plastics. Although the starch in these systems may be broadly classified as a filler, the flexibility allowed in their preparation offers numerous alternatives to conventional fillers. Also, unlike most filler systems, the polymer is covalently bonded to the starch. The synthesis procedures are very simple and may prove to be the most economical method for making plastics from starch. To prepare the graft copolymers, free radicals are initiated onto the starch, either chemically or by irradiation, and then are allowed to react with polymerizable vinyl or acrylic monomers. The choice of free radical initiation method depends on the particular monomer or combination of monomers to be polymerized. Free radical initiation for styrene grafting is best achieved with a cobalt 60 source, whereas ceric ammonium nitrate is more commonly used for grafting acrylonitrile and the acrylates. In essence, the grafting procedure consists of stirring at room temperature for about 3 hr a water slurry of monomer and initiated starch in the absence of oxygen; then the starch graft copolymer is filtered off.

Graft polymerizations have, for the most part, been carried out in water, either with granular, unswollen starch or with starch that has been gelatinized by heating. For grafting onto gelatinized starch, aqueous slurries of starch are heated for 30 min at 85-90°C and then cooled to 25°C prior to adding the monomer. Although gelatinization swells and disrupts starch granules, the polysaccharide is still largely insoluble in the aqueous medium; polymerizations can thus be viewed as taking place onto an insoluble substrate. Only a limited number of polymerizations have been run with water solutions of starch.

Fanta et al. (ref.10) made an interesting observation on the location of grafts within a starch granule that clearly distinguishes these systems from conventional fillers. Scanning electron micrographs of starch-g-polyacrylonitrile made with unswollen starch revealed that grafting took place largely on the surface of the granule with low add-on of 22% graft, whereas with a 44% add-on the grafting took place throughout the granule interior. Similar studies suggest that styrene grafting occurs primarily on the surface of starch granules. These types of studies have not yet been made for the acrylates.

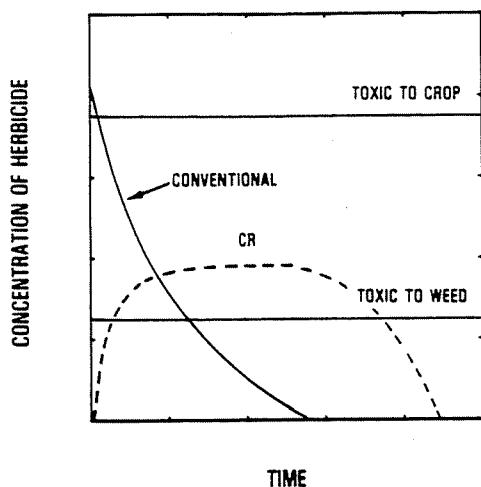


Fig. 3. Idealized release profile for controlled release (CR) of an encapsulated herbicide.

Although melt flow is inhibited by the rigid starch matrix, extrusion processing of starch-g-thermoplastic copolymers will yield continuous plastics, provided the % add-on is about 50% or higher and the extrusion temperature is considerably above T_g of the thermoplastic component. Plastic formation occurs by fusing together individual heat-softened granules of graft copolymer under the high pressures encountered in the extruder die. Scanning electron micrographs of extruded plastics clearly show the fused granule structure (ref.11); the negligible die swell observed in extruded plastics also provides evidence that graft copolymers were never in the molten state.

STARCH-BASED CONTROLLED RELEASE SYSTEM

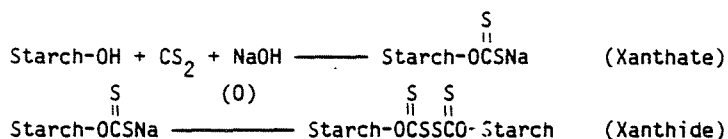
Research at our Center is demonstrating that starch is a promising encapsulating matrix for controlling the release of chemical pesticides to improve safety in handling and to reduce losses of pesticides in the environment due to volatility, leaching, and decomposition by light.

Approaches to the work have required a wide range of both technical and economical considerations. We chose to use approved commercial pesticides and to avoid chemical modifications, such as covalently bonding the pesticides onto starch, because such products would probably require approval as a new pesticide--a very expensive and slow process.

Secondly, for herbicides, the release profile should approach the idealized system illustrated in Fig. 3 (dotted line) under a wide range of field conditions where soil moisture, temperature, pH, and microorganisms vary considerably. Ideally, the herbicide must be released at a rate sufficient to control the target weed but slow enough to avoid phytotoxicity to the crop. Also, because of variations in weather conditions and weed germination rates, an effective level of herbicide must be available for several weeks to avoid multiple

applications, which sometimes are required for conventional formulation. Further demands on the system occur when farmers prefer to apply the herbicide in the fall or to delay soil incorporation. Most conventional formulations now require immediate soil incorporation to reduce losses from evaporation and photodegradation. Finally, research approaches were needed for trapping the pesticide within a starch particle suitable for agronomic applications.

Encapsulation is achieved by incorporating pesticides into an aqueous dispersion of gelatinized starch and then insolubilizing the starch by various crosslinking methods. In our first method, the starch was covalently crosslinked as starch xanthide (ref.12). An alkali dispersion of starch was reacted with carbon disulfide to form starch xanthate (0.1-0.3 DS). Pesticides were emulsified into this dispersion, and then an oxidant was added to crosslink the starch xanthate to an insoluble starch xanthide, which entrapped the pesticide in small cells within granular particles.



Extensive greenhouse and field studies revealed that starch encapsulation greatly reduces evaporation, microbial degradation, photodegradation, and leaching rate of active ingredients over those for nonencapsulated pesticides. Yet, the release of active agent was sufficient to provide adequate pest control. Because of this controlled release, even volatile pesticides do not require immediate soil incorporation.

More recently, we have found that pesticides can be encapsulated by adding either calcium chloride (ref.13) or boric acid (ref.14) to the starch-alkali-pesticide dispersions. Scanning electron micrographs and laboratory release studies indicated that these precipitated starch complexes contain the pesticide trapped in small cells, very much as was found for the xanthide encapsulation. In extensive field and greenhouse studies, these latter products have proven very effective in extending the life of herbicides.

Although there are performance differences between the three classes of products, the borate products are currently emerging as the most feasible because of processing advantages. In contrast to the xanthate process, no carbon disulfide is required. Also, the borate method is conducted with lower levels of water, so that no effluent water must be discharged and the final product contains all of the added pesticide. In both the xanthate and calcium methods, filtrates containing significant amounts of both pesticide and formulating chemicals must be recycled or the chemicals must be removed before the processing water can be discharged into streams.

We are now directing more effort toward release mechanism and factors that affect release of pesticides from the starch-based systems. Moisture is one important factor. Generally, when 1-g samples are wetted with 2-mL portions of water and allowed to dry for 24 h, 5-10% of active agent is released, and this rate of loss will continue with repeated wetting and drying cycles. The method of starch crosslinking appears to have little affect on these release rates. When the products are agitated with more water, especially in the presence of a starch-degrading enzyme, the covalently bonded xanthide system is more stable. For example, when 0.1-g samples were agitated with 2 mL water, buffered to pH 6 for 4 h, 2%, 16%, and 22% of the active agent was released from the xanthide, calcium, and borate products, respectively. With α -amylase present in these systems, nearly 100% of the active agent is released in 1-2 h from the borate and calcium products, but only 14% was released in 4 h from the xanthide product. Release rate also decreases with increased particle size. Efforts are underway to improve methods for determining release rates and to more fully understand the effects of matrix structure on release properties. A better knowledge of these systems would allow design of appropriate formulations for specific applications and greatly enhance acceptance of this technology for broad-scale agronomic use.

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